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Preparation of silver-titanium dioxide core-shell ($Ag@TiO_2$) nanoparticles: Effect of Ti-Ag mole ratio

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Abstract

Silver-titanium dioxide core-shell ($Ag@TiO_2$) nanoparticles were prepared via a reduction reaction of silver nitrate followed by a sol-gel process of titanium tetraisopropoxide (TTIP). The silver core was prepared from 10 ml of 5-mM silver nitrate solution with hydrazine as a reducing agent, and cetyltrimethylammonium bromide as a stabilizing agent. The resulting solution was treated with 1 ml of TTIP solution in ethanol with concentration between 1, 2, 3, 4 and 5 mM (mole ratios of Ti:Ag were 2, 4, 6, 8, and 10 %, respectively). Morphology of the resulting materials was investigated by transmission electron microscope (TEM). The TEM results showed that the core-shell ($Ag@TiO_2$) structure was found only in solutions with low Ti:Ag mole ratio (2-6 %) while the composite morphology with Ag particles randomly embedded in TiO_2 matrix was found with higher Ti:Ag mole-ratio. The $Ag@TiO_2$ particles contain silver core (diameter of 10-15 nm) surrounded by the TiO_2 shell with the shell thickness of 10-20 nm in the solution with 2% mole-ratio and 20-50 nm in that with 6% mole-ratio. Optical spectrometric measurements found that the surface plasmon resonance (SPR) peak of silver nanoparticles was red-shifted from about 410 nm (in solution of silver nanoparticles) to about 425-430 nm (in the solutions of Ag/TiO_2 nanoparticles) and it was not significantly affected by the content of TiO_2.

Keywords: Silver; Titanium dioxide; Silver/Titanium dioxide; Core shell; $Ag@TiO_2$

1. Introduction

Titanium dioxide (TiO_2) has been studied extensively as an effective photo-degradation catalyst. However, TiO_2 is inactive under visible light due to its wide band gap (3.2 eV or λ_{max} ~380 nm). This

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limits the use of TiO_2 as solar or room-light activated catalysts, because the majority of sunlight consists of visible light and infrared radiation, and only about 5% of UV light [1-2]. Several methods have been used to enhance its visible light absorption [3]. These techniques include surface modification via sensitizing organic or semiconductor materials [4-5], band gap modification by creating oxygen vacancies [6-7] or oxygen sub-valency via doping with some nonmetals (such as nitrogen) [7-9] or metals [10-11]. Several works [2-3, 10] found that silver-doped TiO_2 (with metallic silver nanoparticles dispersed in TiO_2 matrix) has absorption in visible region (around 400 nm) and showed significantly enhanced photo-catalysis rate with solar radiation. It was believed that silver-doping does not modify the band gap of TiO_2 but increase catalytic activity by sensitizing through SPR absorption of silver nanoparticles and quick trapping of photo-generated electrons by silver which retards carrier recombination and leaves the holes for degradation reaction of organic species [12-13].

Silver-doped TiO_2 in the form core/shell nanoparticles with silver-core and TiO_2-shell ($Ag@TiO_2$) … The core/shell morphology gives several advantages including well-defined and higher stability of silver nanoparticles (due to its encapsulated state inside TiO_2 shell), ability to tailor absorption band gap of silver sensitizer by changing size of silver-core which can give different SPR absorption peak due to quantum-size effect of silver nanoparticles [14-16]. These could benefit understanding of the photo-catalytic mechanism of the silver-doped titania (Ag/TiO_2).

This paper introduced simple concept to obtain the silver-doped titania in the form core/shell morphology through the sol-gel route by controlling the molar ratio of the titanium and silver starting compounds.

2. Experimental

2.1. Materials and Instrument

All chemicals used in the experiment were analytical (AR) grade. Silver nitrate ($AgNO_3$), hydrazine.monohydrate ($N_2H_2.H_2O$), titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$, TTIP), cetyltriethylammonium.bromide (CTAB), and ethanol were purchased from Sigma-Aldrich Chemicals.

2.2. Preparation of silver nanoparticles and silver-titania nanoparticles

Silver nanoparticles were prepared from $AgNO_3$ via two methods; the common reduction method using hydrazine as reducing agent and CTAB as a stabilizer.[14] Hydrazine solution (2.5 ml, 100 mM) was added into a CTAB solution (100 ml, 1 mM) in an Erlenmeyer flask and stirred for 1 minute. Silver nitrate solution (2.5 ml, 5 mM) was added drop wise into the solution mixture and continue to stir for another 10 minute. The yellow solution of silver Nanoparticles was obtained, as shown in Fig. 1(a).

To prepare silver-titania (Ag/TiO_2) nanoparticles, 10 ml of the freshly prepared solution of silver nanoparticles was treated with 1 ml of TTIP solution in ethanol. Various TTIP concentrations between 1, 2, 3, 4 and 5 mM (mole ratios of Ti:Ag were 2, 4, 6, 8, and 10 %, respectively) was used.

2.3. Characterization Techniques

Transmission electron microscopy (TEM, JEOL model JEM 1220) and UV-visible spectrophotometer (Jusco, model V 530) were used to study morphology of nanoparticles and absorption spectra of the nanoparticles. For TEM measurement, solution of nanoparticles was diluted twice and sonicated. Then,

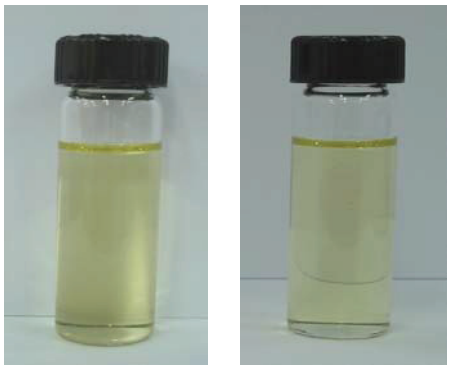
solution was dropped on a holey carbon film supported by a copper grid and allowed to dry in vacuum overnight prior to investigation.

3. Results and Discussion

3.1. Preparation of silver and silver-titania nanoparticles

Silver-titanium dioxide core-shell ($Ag@TiO_2$) nanoparticles were prepared via a reduction reaction of silver nitrate (a Ag precursor) followed by a sol-gel process of TTIP (a titania precursor). Hydrazine was used as reducing agent, CTAB as a protecting agent for nanoparticles, and ethanol as a solvent for TTIP.

Solution of the synthesized silver nanoparticles was clear, yellow in color (as shown in Fig. 1a). After treating with TTIP at various Ti:Ag mole ratio (2 – 10%), the obtained silver-titania solutions were found to have a yellow color (with a slightly lighter color) similar to that of the silver core (see for example in Fig. 2b). Change in the amount of TTIP (from 2 to 10% molar ratio) did not significantly affect the color of the solutions.



(a) **(b)**

Fig. 1. Photographs of the solutions of (a) silver nanoparticles (b) $Ag@TiO_2$ nanoparticles (Ti:Ag = 2% mole)

3.2. Morphology of the silver and silver-titania nanoparticles

TEM micrographs of silver nanoparticles and the resulting silver-titania nanoparticles are shown in Fig. 2. The micrograph indicated that the silver nanoparticles (Fig. 2a) were spherical with their size of about 5 - 15 nm.

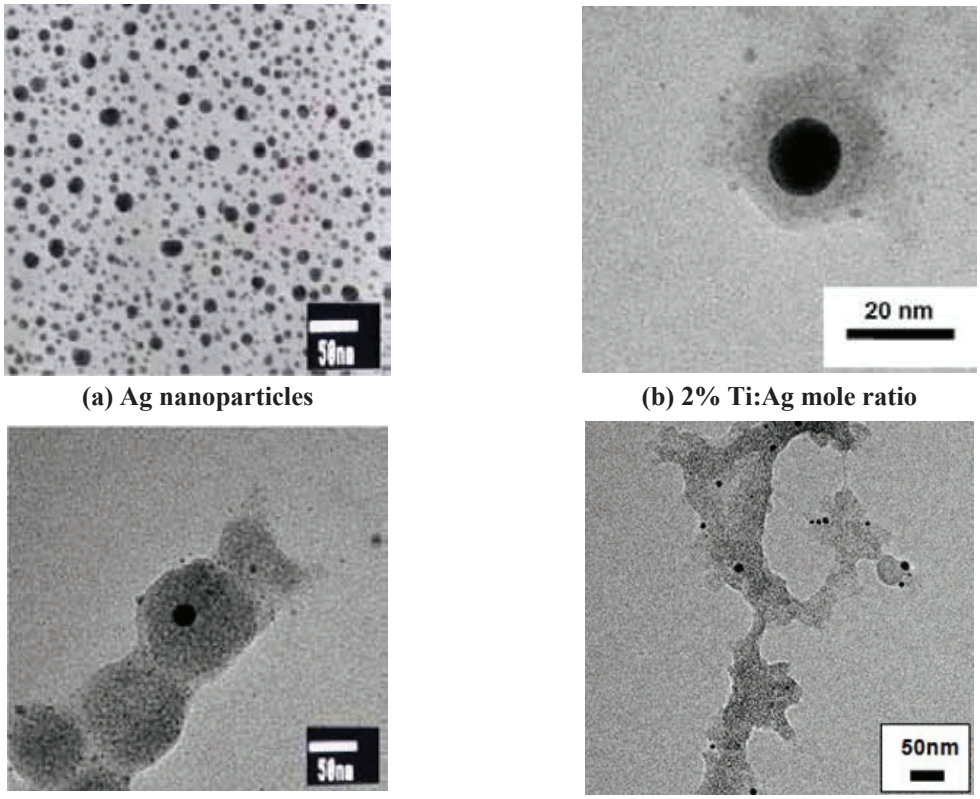
The silver-titania nanoparticles were shown in Fig. 2b-d. It can be seen that the core/shell morphology was obtained at the low (2 and 6%) Ti:Ag mole ratio. The Ag@TiO_2 nanoparticles at 2% mole ratio (Fig. 2b) had a silver-core diameter of about 10-15 nm and titania shell thickness of about 8-15 nm. The core/shell particles at 6% mole ratio (Fig. 2c) had thicker titania shell (of about 20 – 50 nm).

The composite morphology with Ag particles randomly distributed in titania matrix was found at the high (10%) mole ratio. There were large titania aggregates (most of them are larger than 50 nm) where silver nanoparticles can be embedded inside.

The effect of Ti:Ag mole ratio on silver-titania morphology can be explained in term of the available nucleation sites and growth of titania particles on the pre-existing surface of silver nanoparticles. At low concentration of titania precursor, titania can effectively nucleated on surface of silver nanoparticles and this leads to the core/shell morphology. With higher concentration of titania precursor, more titania can grow around silver particles forming the core/shell particles with larger shell thickness. However, with a too high concentration, many titania precursors cannot find the available silver surface to nucleate and they form self-aggregation and jointed particles between the grown core/shells. This situation leads to the composite morphology with Ag nanoparticles embedded in titania matrix (which seems like Ag particles deposited in the titania matrix). The schematic diagram on Fig. 3 illustrates the change in Ag/TiO_2 morphology from the core/shell to the composite one as the Ti:Ag mole ratio is increased.

3.3. Optical property of the silver-titania nanoparticles

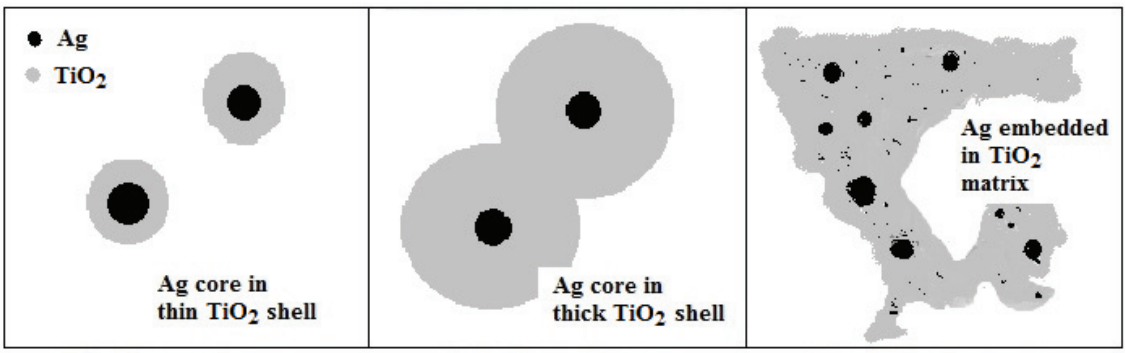
Visible spectra of silver and silver-titania nanoparticles are shown in Fig. 4. The maximum absorption wavelength around 400 – 440 nm found in every spectra corresponds to the localized surface plasmon resonance (LSPR) of silver nanoparticles [15-16]. LSPR originates from the collective oscillation of electron at the surface of silver nanoparticles and the SPR peak location can be largely modified by the changes in size and shape of the nanoparticles as well as the change in dielectric environment surrounding the nanoparticles [14-15]. The results in Fig. 4 show that the LSPR peak of Ag/TiO_2 nanoparticles red-shift (from 411 nm for the silver core alone) to higher wavelength (425 - 428 nm in silver-titania nanoparticles). The red-shifts is the results of the change in dielectric environment around silver nanoparticles since titania has a much higher refractive index (~ 2.5) as compared to a low value of silver (~ 0.15) and the solvent used (~ 1.3 for water and alcohol). An increase in Ti concentration from 2 to 10 % mole ratio does not cause more red-shift. This is because the titania shell is so thick (> 20 nm) that an increased thickness is too far away from the LSPR field at the silver interface. Therefore, the Ti:Ag mole ratio, though causing morphology change, does not significantly affect the optical property of Ag/TiO_2 nanoparticles.



(a) Ag nanoparticles (b) 2% Ti:Ag mole ratio

(c) 6% Ti:Ag mole ratio (d) 10 % Ti:Ag mole ratio

Fig. 2. TEM micrographs of Ag/TiO_2 nanoparticles at various Ti:Ag mole ratios (a) at 2% mole ratio; (b) at 6% mole ratio; (c) at 10% mole ratio



(a) 2% Ti:Ag mole ratio (b) 6% Ti:Ag mole ratio (c) 10 % Ti:Ag mole ratio

Fig. 3. Schematic diagram Ag/TiO_2 morphology at various Ti:Ag mole ratios (a) Ag core in thin TiO_2 shell at 2% mole ratio; (b) Ag core in thick TiO_2 shell at 6% mole ratio; (c) Ag embedded in TiO_2 matrix at 10% mole ratio

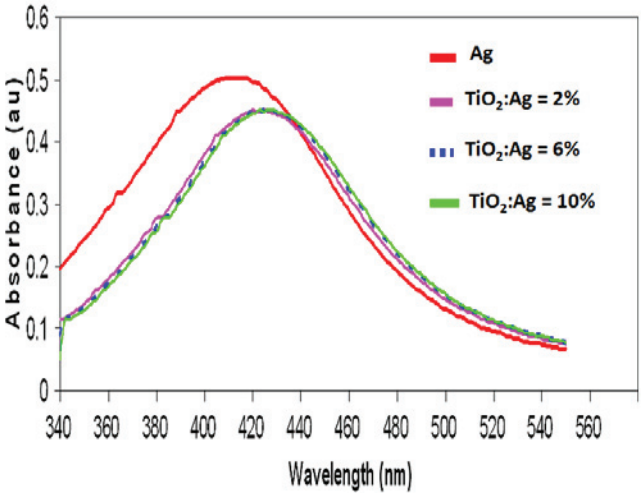


Fig. 4. UV-visible spectra for solutions of silver nanoparticles and Ag/TiO_2 nanoparticles

4. Conclusion

Silver-titanium dioxide core-shell nanoparticles were prepared via a reduction reaction of silver nitrate followed by a sol-gel process of titanium tetraisopropoxide. We found that mole ratio of Ti:Ag is an important factor in controlling morphology of the resulting Ag/TiO_2 nanoparticles. The core-shell morphology of $Ag@TiO_2$ can be obtained only at low Ti:Ag mole ratio (2-6%), with the thicker TiO_2 shell as the higher Ti mole ratio. At high Ti:Ag mole ratio (> 6%), the composite morphology with Ag particles randomly embedded in TiO_2 matrix was formed. The presence of TiO_2 shell changes dielectric environment around Ag nanoparticles and causes the red shift of silver's SPR peak but an increase in Ti:Ag mole ratio does not significantly affect the optical property of Ag/TiO_2 nanoparticles.

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